Pools and solubility of soil phosphorus as affected by liming in long-term agricultural field experiments

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ABSTRACT

Published laboratory studies suggest minimum solubility of soil phosphorus (P) in the pH range traditionally considered as the target for lime applications on agricultural land. However, the potential significance of these results for the timescale relevant in practical agriculture remains to demonstrate. We revisited four long-term (50–76 years) agricultural lime experiments located on Quaternary deposits with topsoil texture ranging from silt loam to silty clay and initial pH between 5.0 and 6.0. Crop uptake data and desorption experiments in the laboratory indicated that liming enhanced the solubility of P added with fertiliser in the decades following the application of lime. An empirical mass-balance model demonstrated that changes in acetate-lactate extractable P ('P-AL'), previously shown to be related to reactive phosphate adsorbed on soil mineral surfaces, was proportional to field P balances (fertiliser P – harvested P) and inversely proportional to the net proton load to the soil. Extraction data suggest that liming enhanced the incorporation of silica in non-crystalline sesquioxides, which in turn inhibited the conversion of fertiliser P into less extractable forms by migration of P to inside the oxides. Liming induced a lowering of the C/N ratio in one of the experiments, suggesting stimulated decomposition of soil organic matter. However, lime applications did not lead to a decline in the pool of soil organic P, as measured by the combustion method. Mass-balance considerations showed that changes in organic-matter input due to liming were unlikely to result in observable changes in the pool of soil organic P.

1. Introduction

One of the purposes of applying lime to agricultural fields is to enhance the availability of phosphorus (P) to crops (e.g., Havlin et al., 1999). However, seemingly in conflict with the traditional theory on P solubility, previous and recent studies indicate that in several soils, the solubility of soil P exhibits a minimum rather than a maximum at slightly acidic or circumneutral pH (Murrmann and Peech, 1969; Weng et al., 2011; Gustafsson et al., 2012; Eriksson et al., 2016a). Barrow (2017) argued that an obsolete conception of the mechanisms responsible for P-solubility control leads to incorrect predictions concerning the availability of P following a pH change in the soil, and concluded that raising the pH to 6 or 7 is not likely to enhance P availability to crops. However, the cited studies were based on laboratory experiments, where the pH was adjusted by adding acid or base to a soil-water slurry. Few if any studies have tested whether the observations from such studies are relevant for the agricultural field, which is an open system with inputs and outputs of P, where effects of

liming may persist for several years or decades.

As to the chemistry of inorganic soil P, water extracts of agricultural soils are commonly in disequilibrium with known P-bearing mineral phases (Devau et al., 2009, 2011; Weng et al., 2011; Gustafsson et al., 2012; Eriksson et al., 2016a), therefore adsorption is generally considered to be the primary mechanism controlling P solubility in soil (Murrmann and Peech, 1969), with the caveat that precipitation of Ca phosphates may occur at high pH (Haynes, 1982). In experiments with high additions of P, Al phosphates may also precipitate (Veith and Sposito, 1977). The theory of adsorption on oxide surfaces predicts that the solubility of phosphate and other oxyanions decreases when the soil is acidified, until pH approaches the pK_a of the anion; protonation of the latter makes it less prone to forming surface complexes if pH decreases further (Sposito, 1989, ch. 8; Cabrera et al., 1977; Raven et al., 1998). Hence, maximum adsorption (minimum solubility) of P occurs at around pH 4 for Al or Fe oxides (e.g., Cabrera et al., 1977; Nagar et al., 2010), allophane (Oh et al., 1999) and kaolinite (Chen et al., 1973; Edzwald et al., 1976; Manning and Goldberg, 1996). For clay

Table 1
Site locations, texture and approximate initial or earliest available soil chemistry of the field experiments.

Alias for this paper	Series	Experiment ID	Coordinates	Run during	Soil texture	pH (H₂O)	CEC_{pH7} $(cmol_c\ kg^{-1})$	Calcium saturation (% of CEC_{pH7})	P-AL $(mg\ kg^{-1})$[a]	P-HCl $(mg\ kg^{-1})$[b]
Röbäcksdalen	R3-1002	AC-2-1962	63.8086°N 20.2459°E	1962–present	Silt loam[c]	5.0[d]	11[d]	40[d]	48[d]	710[d]
Västra Eknö	R3-1002	U-3-1962	59.4378°N 15.9939°E	1962–2011	Silty clay[c]	5.2[d]	20[d]	50[d]	30[d]	830[d]
Lanna-1936	R3-1001	R-29-1936	58.3485°N 13.1276°E	1936–present	Topsoil of silty clay loam on subsoil of clay (from approx. 30 cm)[e]	6.0[f]	19[g]	n.a.[h]	n.a.[i]	n.a.[i]
Lanna-1941	R3-1001	R-27-1941	58.3448°N 13.1174°E	1941–present		5.9[f]	20[g]	n.a.[h]	n.a.[i]	n.a.[i]

[a] Phosphorus extracted by 0.4 M acetic acid + 0.1 M ammonium lactate pH 3.75 (Egnér et al., 1960); 40–80 mg kg^{-1} is considered the 'medium' range according to Swedish extension standards, whereas values < 20 mg kg^{-1} belong to the poorest category in a five-degree scale (see also Jordan-Meille et al., 2012).

[b] Phosphorus extracted by 2 M HCl at 100 °C.

[c] Unpublished data from 1986 of G. Simán.

[d] Simán (1985); Ca saturation used as an estimate of base saturation.

[e] Texture of the adjacent field 'Skifte I' (Johansson, 1944).

[f] Control plots in 1971 (Lanna-1936) and 1969 (Lanna-1941).

[g] Control plots in 1983 (Lanna-1936) and 1985 (Lanna-1941).

[h] Early data not available.

[i] Initial values unavailable at Lanna; present overall ranges: P-AL 13–66 mg kg^{-1}; P-HCl 330–560 mg kg^{-1}.

minerals with a permanent negative charge, maximum adsorption usually occurs at a considerably higher pH of around 6–7 (Chen et al., 1973; Manning and Goldberg, 1996). The modelling of Devau et al. (2009, 2011) suggested that permanent-charge clay minerals, if abundant in the soil, might dominate P sorption at neutral and slightly alkaline pH. However, a re-evaluation of their modelling indicates that hydrous oxides remain a dominant sorbent under these conditions as well (Weng et al., 2011; Lumsdon, 2012; Gustafsson and Lumsdon, 2014). In practice, P solubility can therefore be expected to decline with soil pH.

Binding of inorganic phosphate in soil may not be correctly understood as simple adsorption onto mineral surfaces. Barrow (1983) developed a model to show that the sorption can be described as a combination of fast adsorption on external surfaces and kinetically restrained diffusion of phosphate in the lattice of the adsorbent. This mechanism might explain the commonly observed increase in dissolved-P concentration upon addition of acid to soil-water slurries, if P simply dissolves along with a part of the hydrous Al-oxide phases, in which it is occluded (Murrmann and Peech, 1969). Also in the field, the amount of adsorbent present in a soil is likely to change, modifying the sorption properties of the soil over time. Thus, in B horizons of acidic forest soils, Grand and Lavkulich (2015) found that conditions that favour precipitation of short-range order Al phases reduce the lability of soil P. McGahan et al. (2003) demonstrated that acidification induced by agricultural practices increases the formation of short-range order mineral phases with Al and Fe. It may therefore be hypothesised that proton-driven weathering of primary minerals leads to occlusion of P by secondary minerals. After liming, the base-saturated exchange complex might adopt the role of a proton sink, thereby reducing silicate weathering and occlusion of P in secondary mineral phases.

The pool of soil organic P appears to be insensitive to applications of fertiliser or manure in the long term (Negassa and Leinweber, 2009; Ahlgren et al., 2013; Bergström et al., 2015). However, there are limited data on the long-term effects of liming on soil organic P under field conditions. Liming may both enhance the rate of mineralisation and the rate of harvest-residue input to the soil, due to an increased crop production, and the net effect on the soil organic matter pool is difficult to generalise (Paradelo et al., 2015). At the molecular level, several studies indicate that the P mineralisation rate is controlled by the activity of specific enzymes produced by bacteria or fungi in the soil (Tarafdar and Jungk, 1987; McLatchey and Reddy, 1998; Chen et al., 2002). The activity of these enzymes is influenced by substrate availability, soil humidity, temperature and pH (Martínez, 1968; Haynes and Swift,

1988; Šarapatka, 2003; Nannipieri et al., 2011). Phosphatases are denominated 'acid' or 'alkaline' depending on their different optimal pH with regard to enzyme activity (Eivazi and Tabatabi, 1977; Margesin and Schinner, 1994; Ekenler, 2002). Similarly, phytases are referred to as acid, neutral or alkaline (Wyss et al., 1999; Mullaney and Ullah, 2003). Phosphodiesterases exhibit a high activity in a wide range of pH values (4.5–9.5) (Nannipieri et al., 2011). Since P mineralisation involves a wide variety of enzymes, each having its particular optimum pH, the net effect of a change in pH is difficult to predict. However, Halstead et al. (1963) found a positive effect of liming on the mineralisation of organic P in acidic soils from Canada. Similarly, Trasar-Cepeda et al. (1991) used Ca(OH)₂ to adjust the pH of an Andisol and found that the turnover of organic P significantly increased in soils receiving the highest dose of base. It may therefore be hypothesised that liming depletes the stocks of organic P in a soil.

The objective of the present investigation was to examine P solubility on different time scales, based on data and soil materials obtained from long-term agricultural field experiments that had received lime and P fertiliser during 50–76 years. We also assessed the pool of organic P using a standard method. The following hypotheses were raised:

1. Long-term effects on P solubility, obtained after liming in the field, are distinct from the effects observed after adjustment of pH in short-term incubations in the laboratory.
2. In the long term, liming enhances P availability by inhibiting the occlusion of P in short-range order mineral phases.
3. Liming enhances the mineralisation of soil organic P, resulting in a decreased stock of organic P in the long term.

2. Materials and methods

2.1. Sites and field experiments

Two series of field experiments were used: the Permanent Liming Trials (series R3-1002) represented by two sites, one at Röbäcksdalen in northern Sweden and the other at Västra Eknö in east-central Sweden (Table 1), and two of the Long-Term Liming and Phosphorus Trials (R3-1001) at the Lanna experimental station in south-west Sweden.

At Röbäcksdalen, the bedrock is dominated by migmatised (metamorphic) sediments of greywacke and argillite with elements of granite-granodiorite and pegmatite (SGU, 1989). The experiment is situated on a fluvial plain with clayey-silty sediments that settled in a post-glacial marine environment 270 m below the postglacial marine limit and